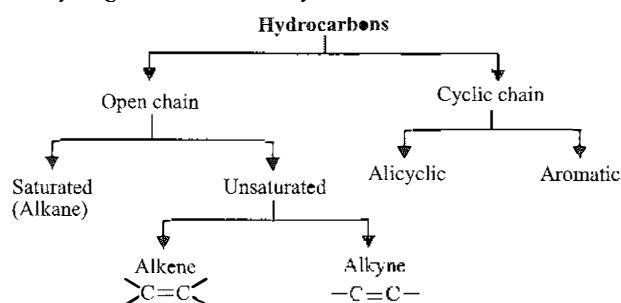


Unit 13

Hydrocarbons

- Organic compounds composed of only carbon and hydrogen are known as hydrocarbons.



ALKANES

- General formula C_nH_{2n+2}
- Due to inertness known as paraffins.
- Only C – C and C – H single bonds are present.
- All carbons are sp^3 hybridised.

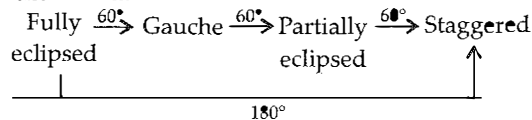
Isomerism

- Structural isomerism** : Alkanes exhibit only chain isomerism. Methane, Ethane, Propane do not exhibit isomerism.

Alkane	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}
No. of possible isomers	2	3	5	9	18

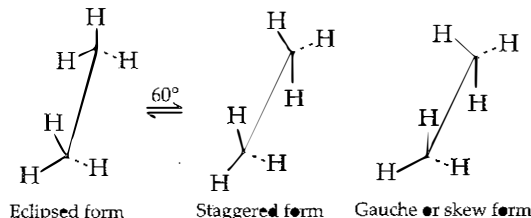
Conformations

- The different arrangement of atoms in space that results from free rotation of groups about C – C bond axis are called conformational isomers or rotational isomers and this phenomenon as conformational or rotational isomerism.
- Fully eclipsed conformation** : In this form the bigger atoms are nearest to each other. These conformers have maximum energy and minimum stability.
- Staggered form** : In this form the bigger atoms are farthest to each other. These conformers have minimum energy and maximum stability.
- Gauche or skew** : Rotation between 0° to 60° generates one of the many arrangements in between staggered and eclipsed forms. These arrangements are called Gauche or skew form.



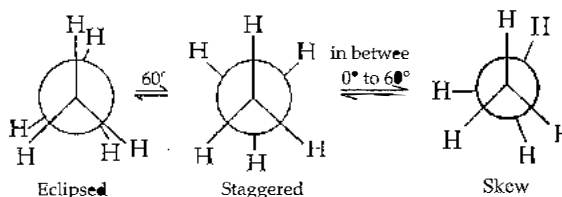
Sawhorse Projection

- It is a view of molecule down a particular C – C bond, and groups connected to both the front and back carbons are drawn using sticks at 120° angle. The left-hand bottom end of this locates atoms nearer to the observer and right-hand top end atoms that is further away.



Newman Projection

- In Newman projection, the two carbon atoms forming the σ -bond are represented by two circles, one behind the other, so that only front carbon is seen. The hydrogen atoms attached to the front carbon are shown by the bonds from the centre of the circle while the atoms attached to the back carbon are shown by the bonds from the circumference.



Conformations of Ethane ($CH_3 - CH_3$)

- An infinite number of conformations (relative arrangement of hydrogen atoms) are possible for ethane, if one of the methyl groups is rotated along the C – C axis keeping the rest of molecule undisturbed.
- Eclipsed conformation** : In this conformation rotation about C – C single bond is by an angle such that hydrogen atoms of front carbon atom completely cover or eclipse the hydrogen atom of rear carbon atom i.e., only three hydrogen atoms of front carbon are visible. This conformation is most unstable.
- Staggered conformation** : In this conformation rotation about C – C single bond is by an angle so that hydrogen atoms of two carbon atoms are at maximum distance from each other making it stable by 2.9 kcal/mol as compared to eclipsed conformation.

Hydrocarbons

- Skew conformation** : The infinite number of possible intermediate conformations between the two extreme conformations (eclipsed and staggered) are referred to as skew conformations.

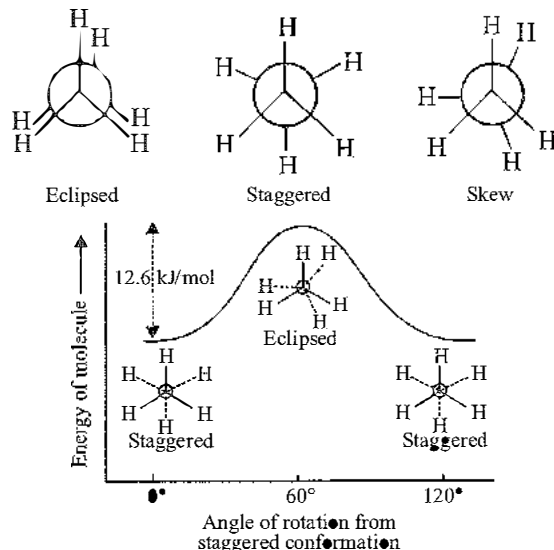
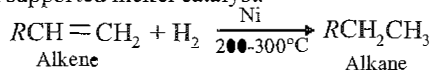


Fig. : Degree of rotation from the staggered form and energy of the molecule of ethane.

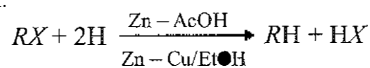
Methods of Preparation

- Hydrogenation of unsaturated hydrocarbons (Sabatier and Senderen's reactions)** : The method involves the reduction of unsaturated hydrocarbons (alkenes and alkynes) with nickel catalyst. Raney nickel is more reactive than supported nickel catalyst.

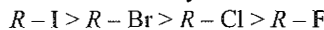


Pt or Pd can also be used as catalyst for above reactions. This method cannot be used for the preparation of methane CH_4 .

- Reduction of alkyl halides** : Alkyl halides can be reduced with zinc and acetic acid or zinc-copper couple in ethanol.



Order of reactivity of different alkyl halides is :



Reduction can also be carried out by LiAlH_4 .

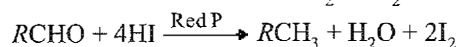
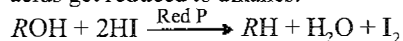
1° and 2° alkyl halides are readily reduced by LiAlH_4 but 3° halides give mainly alkenes.

NaBH_4 reduces 2° and 3° halides but not 1° halide.

Alkyl iodides are conveniently reduced to alkane by heating with red phosphorus and HI.

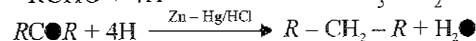
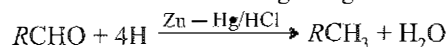


- Reduction of alcohols, aldehydes, ketones, fatty acids and their derivatives** : On heating with HI and red P at 425 K in a sealed tube, alcohols, aldehydes, ketones and acids get reduced to alkanes.

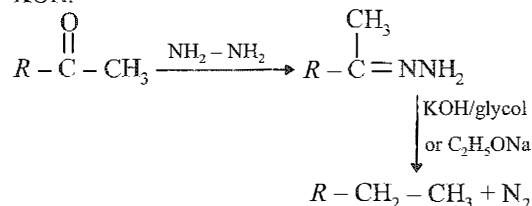


Aldehydes and ketones can be reduced by other alternative methods also.

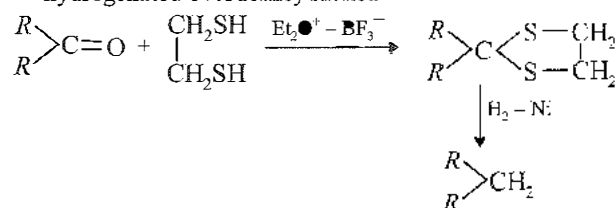
- Clemmensen reduction** : In this method aldehydes and ketones are reduced with Zn - Hg amalgam and conc. HCl.



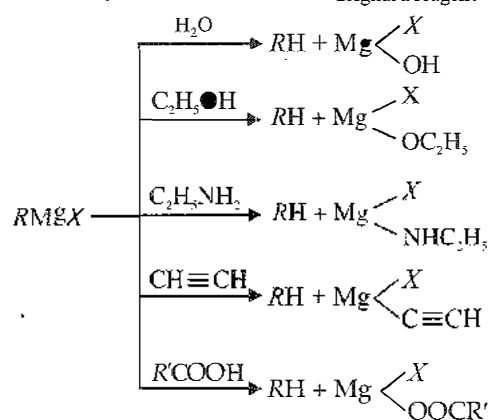
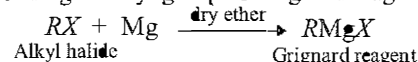
- Wolff-Kishner reduction** : In this method aldehydes and ketones are reduced with hydrazine ($\text{NH}_2\text{-NH}_2$) and KOH.



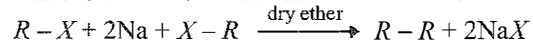
- Mozingo method** : In this method, the carbonyl compound is converted into its dithioacetal or ketal using ethanedithiol in the presence of a Lewis acid. Dithioacetal is then hydrogenated over Raney nickel.



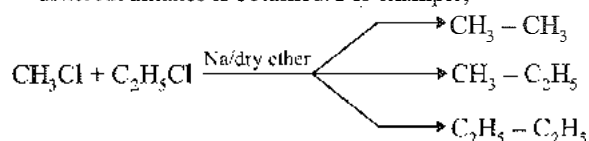
- Decomposition of Grignard reagent** : Grignard reagent (RMgX), an organometallic compound on reaction with active hydrogen (hydrogen attached to strongly electronegative atom like O, N, S or F) compounds like H_2O , ROH , RNH_2 , RCO_2H , $\text{RC}\equiv\text{CH}$, etc. decompose to give alkane corresponding to alkyl group of Grignard reagent.

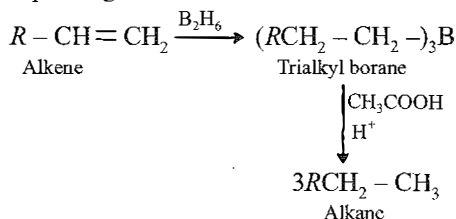
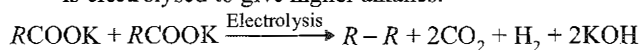
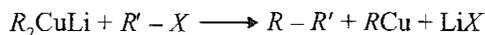
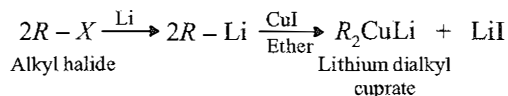
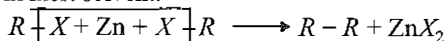


- Wurtz reaction** : In this reaction ether solution of alkyl halide is treated with sodium to form alkane.



This method is useful with single type of alkyl halide. If two different alkyl halides are used a mixture of three different alkanes is obtained. For example,

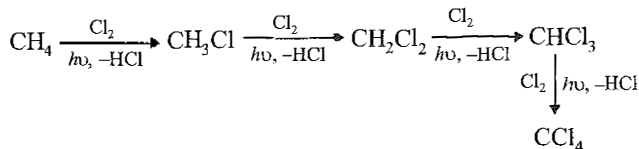




Physical Properties

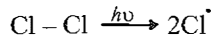
- **State :** $C_1 - C_4$ odourless, colourless gases
 $C_5 - C_{17}$ odourless, colourless liquids
 C_{18} onward odourless, colourless solids
- **Density :** Increases very slowly with increase in molecular mass.
- **Solubility :** Insoluble in polar solvents, soluble in non-polar solvents.
- **Boiling points :** Boiling point of normal alkanes increases regularly with number of carbon atoms.
 Normal isomers have higher boiling point than the branched chain isomer. Greater the branching, lower will be the boiling point.
- **Melting points :** Alkanes with even number of C-atoms have higher m.pt. than the last lower and next higher alkane having odd number of C-atoms.

Chemical Properties

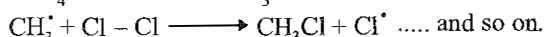
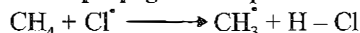


Mechanism

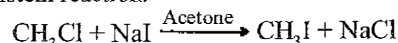
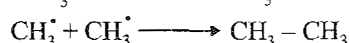
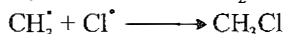
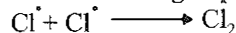
➤ **Chain initiation step :**



➤ **Chain propagation step :**

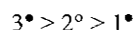


➤ **Chain terminating step :**

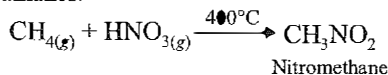


- Reactivity and Selectivity :** For a particular type of abstraction of H (say 1°) reactivity of halogens is in order:
 $F_2 > Cl_2 > Br_2 > I_2$

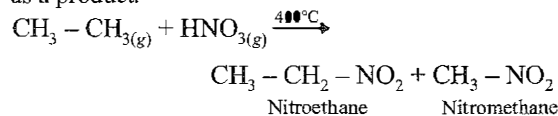
For a given halogen, abstraction of 1°, 2°, 3°, hydrogen follows the order:



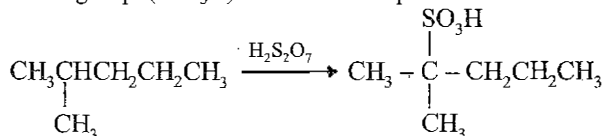
Bromine is less reactive than chlorine towards alkanes but bromine is more selective in the site of attack when it reacts.



Vapour phase nitration causes cleavage of C-C and C-H bond resulting in the formation of mixture of nitroalkanes as a product.



- **Sulphonation** : Replacement of hydrogen atom by sulphonic acid group ($-\text{SO}_3\text{H}$) is known as sulphonation.



The ease of replacement of hydrogen atom is $3^\circ > 2^\circ > 1^\circ$.
Sulphonation also follows free radical mechanism.

- **Reed's reaction or chlorosulphonation of alkanes :** Alkanes undergo chlorosulphonation on treatment with a mixture of sulphur dioxide and chlorine in presence of ultraviolet light to form alkanes sulphonyl chlorides.

